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REVERSION STUDIES OF NATURAL AND GUAYULE RUBBERS

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ABSTRACT

The main objective of this work was to compare the curing and reversion (loss of mechanical properties) characteristics of sulfur-cured guayule rubber with that of natural rubber. A series of formulated natural and guayule rubber compounds was studied by employing Fourier transform infrared spectroscopy and mechanical spectroscopy to characterize the cure and reversion behavior. The reversion process was found to be dependent on the amount of trans-methine structure formed during and after vulcanization. The appearance of this molecular species coincided with the onset of mechanical reversion.

Two variables affecting the cure and reversion process were studied: the amount of carbon black loading, and the temperature of cure. It has been observed that reversion and $G'(max)$ are significantly affected by carbon black loading. An increase in carbon black loading showed a decrease in reversion and an increase in $G'(max)$. As the cure temperature was increased, an increase in reversion was detected. In general, guayule rubber exhibited a slower rate of reversion than natural rubber; however, natural rubber exhibited a larger modulus than guayule rubber.

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INTRODUCTION

In recent years much interest has been shown in the cultivation deresination and processing of the guayule shrub (Parthenium argentatum) to yield guayule rubber. The development of guayule rubber as a domestic source of natural rubber is facilitated by the predictions that the world will face a severe shortage of natural rubber by the end of the decade. This reasoning prompted comparisons between guayule rubber and natural rubber (Hevea brasiliensis). The eventual goal is to replace, in certain instances, the imported natural rubber with its domestic counterpart, guayule rubber.

The main objective of this work was to compare the reversion characteristics in the accelerated sulfur curing of guayule rubber with that of natural rubber. A series of formulated natural rubber and guayule rubber compounds were studied using a sulfur accelerated curing system. Quantitative studies of the compounding variables which affect the reversion process have been investigated. A comparison between guayule and natural rubber has been carried out and revealed that guayule rubber may serve to be more than an adequate replacement for natural rubber.

If guayule rubber is to be treated as a genuine replacement for natural rubber it must meet or surpass the physical properties previously measured for natural rubber. Therefore, various compounding and physical property testing must be carried out to provide valuable information on curing rates, optimum cure temperature, maximum storage modulus, and tensile strength.[1-3]

Limitations for any rubber system exist where higher curing rates at high temperatures are usually not equivalent to those obtained at longer cure times at lower temperatures. At elevated temperatures this is usually manifested by a decrease in the dynamic storage modulus. An even greater limitation results from the phenomenon known as reversion (a loss of mechanical properties). Reversion is postulated to occur when the initially formed mono, di-, and polysulfidic crosslinks[4] degrade through a process known as desulfurization. When desulfurization is faster than the crosslinking reaction, reversion occurs.[5,6] This causes physical and mechanical properties such as tensile strength, stiffness, and tear resistance to deteriorate.

In order to produce a high quality compound, the effects pertaining to the amount of accelerator, filler, and the selection of the proper curing system on the extent of reversion should be addressed.

EXPERIMENTAL

Materials

Natural rubber (SMR-20) was used as the base material for all formulations with natural rubber as its primary stock. This material was supplied by the Goodyear Tire and Rubber Company of Akron, OH. The guayule rubber was obtained from the Firestone Tire and

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Rubber Company. This material was grown in Arizona and processed at the Firestone processing facility in Sucaton, Arizona. The rubber was separated from the plant tissue by a series of extractions with acetone.

The formulations used were made up of 100 parts rubber, two parts sulfur, two parts Sanctocure (N-cyclohexyl-2-benzothiazyl-2-sulfenamide), five parts Zinc Oxide, two parts stearic acid, one part Agerite Resin D (poly (1,2-dihydro-2,2,4-trimethylquinoline)) and zero, 20, and 40 parts N 220 carbon black.

The formulated rubbers were prepared by mixing the ingredients in a Haake-Buchler Rheocord System 40 internal mixer. The internal temperature remained constant at 80°C for approximately 30 minutes. The rotor speed was 60 rpm. Samples were stored in the refrigerator when not in use to inhibit premature curing.

Characterization Techniques

A Rheometrics mechanical spectrometer model 7700 with rotational cone disks was used to monitor G', the dynamic storage modules, a measure of the rubber elasticity or stiffness. As the cure proceeds, G' increases with increasing network formation. The amount of reversion can then be calculated with the equation:

$$\% \text{ Reversion} = \{[G'(max) - G'(t)]/G'(max)\} \times 100 \tag{1}$$

where G'(max) is the maximum dynamic storage modulus and G' is the dynamic storage modulus of reversion following G'(max).

Samples were obtained using cast rubber films from toluene solution. Rubber samples were dissolved in spectral grade toluene and deposited on a KBr salt plate. The solvent was evaporated and another KBr salt plate was placed over the original one. The KBr sandwich was then placed in an isothermally heated cell which remained at the prescribed temperature for the entire cure process. Spectra were taken at various time intervals.

The infrared spectra were collected on a Perkin-Elmer Model 1550 Fourier transform infrared spectrometer controlled by a Model 7500 Perkin-Elmer computer. The spectra were then stored on 5-1/4 inch floppy disks for further data reduction.

A Waters ALC/GPC-244 instrument with a 600 A solvent delivery system, 660 solvent programmer and 440 UV absorbance detector was used for GPC analysis.

Solutions were prepared by dissolving two grams of rubber into one liter of tetrahydrofuran. The resultant solution had a concentration of 0.20 g/dl.

RESULTS AND DISCUSSION

Gel Permeation Chromatography

The results from GPC reveal that the average MW for the guayule rubber sample was approximately 800,000 g/mol. The natural rubber gum stock used had an average MW of approximately 2.5×10^6 g/mol. These MW values are relative to polystyrene standards.

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Mechanical spectrometry

The major factor affecting the reversion of guayule rubber is the temperature at which the cure is carried out. Figure 1 shows the mechanical spectrometer data for guayule rubber at five different temperatures. The time to reach G'(max) is significantly decreased with increasing temperature. Even the magnitude of G'(max) is affected by the cure temperature as it decreases with increasing temperature. The vulcanizates cured at 130°C and 140°C show no reversion, while reversion increases considerably with increasing temperature. In the sample cured at 130°C, no reversion is detected even after two hours. Such extended cure times are of no commercial use, so compromises must be reached where a maximum G' is obtained in a minimum timeframe. This trend also holds true for the natural rubber curing system studied.
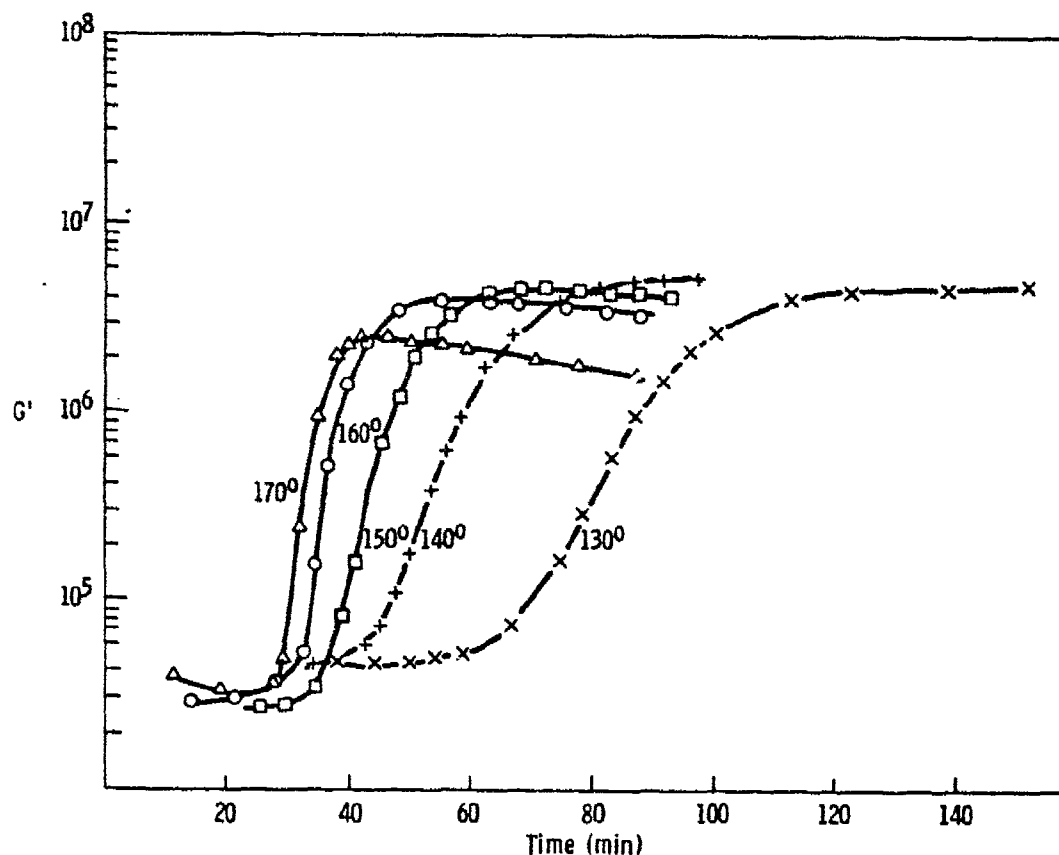
Figure 1. Rheometer cure curve for guayule rubber at five different temperatures.

Figure 2 shows a comparison of the cure curves from the mechanical spectrometer for natural rubber and guayule rubber with 20 pphr carbon black at 150°C. In general, both rubbers show similar scorch times (time at which increase in G' is detected); however, the maximum G' is greater for natural rubber than guayule rubber. This is probably indicative of the previously existing crosslinks in the gum stock of the natural rubber.

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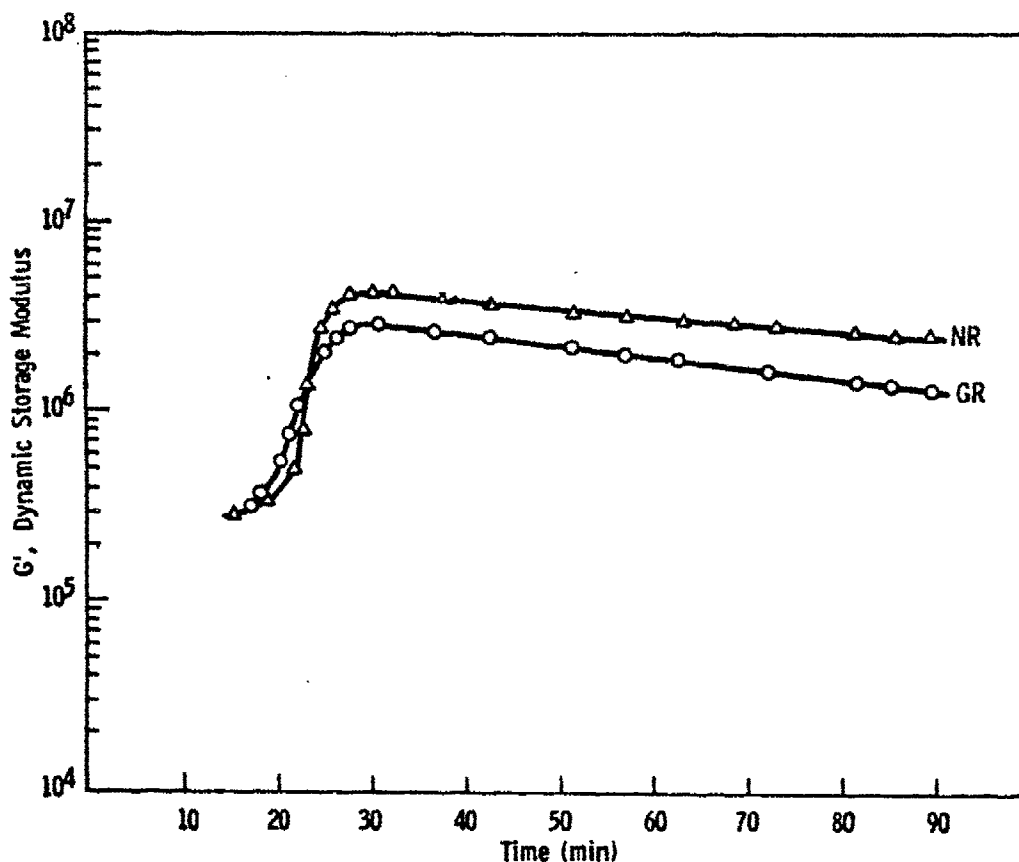
Figure 2. Comparison rheometer cure curves for natural rubber and guayule rubber at 150°C.

After $G'(max)$ is attained, a slow decrease in the modulus is detected. This is the onset of the reversion process. Both natural rubber and guayule rubber exhibit reversion which is attributed to the uncrosslinking of the S-S bonds formed during vulcanization. The natural rubber sample exhibited 50% reversion after 60 minutes while the guayule rubber sample exhibited 45% reversion.

Compounding additives play a major role in the curing chemistry of these rubbers. Of particular interest is the amount of reinforcement obtained by the addition of carbon black. Reinforcement is second only to vulcanization temperature as the most effective process used to enhance the mechanical properties of rubber. An increase in reinforcement increases stiffness, modulus, tear strength, and abrasion resistance.

Figure 3 shows a plot of ln $G'(max)$ versus carbon black loading for both guayule and natural rubbers. The plots for both are linear with the guayule rubber showing a slightly lower $G'(max)$ at the lower carbon black loadings. However, at the higher carbon black loadings, both show similar $G'(max)$ values.

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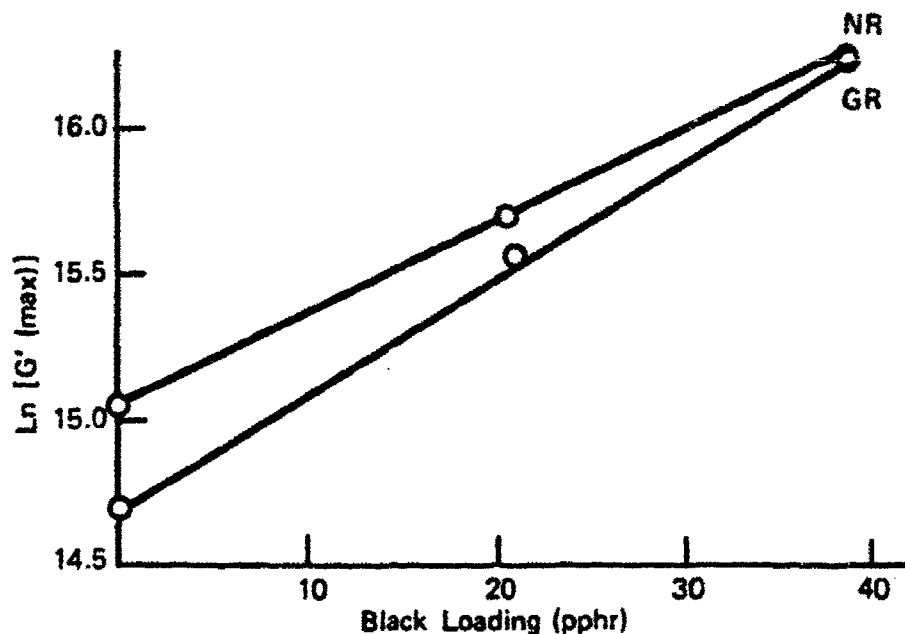
Figure 3. Comparison between natural rubber and guayule rubber
showing the ln G'(max) versus the carbon black loading.

The amount of reversion was found to be dependent on the carbon black concentration. In fact, significant improvement can be seen in the reversion resistance of both rubbers when carbon black is added. Figure 4 shows this improvement. Figure 4 also illustrates that the % Reversion is not a linear function of black loading. The most significant reduction of the reversion provided by carbon black occurs after the initial 10 pphr loading. More importantly, Figure 4 demonstrates the fact that the guayule rubber exhibits less reversion at all carbon black loading levels than natural rubber.

% REVERSION VS CARBON BLACK
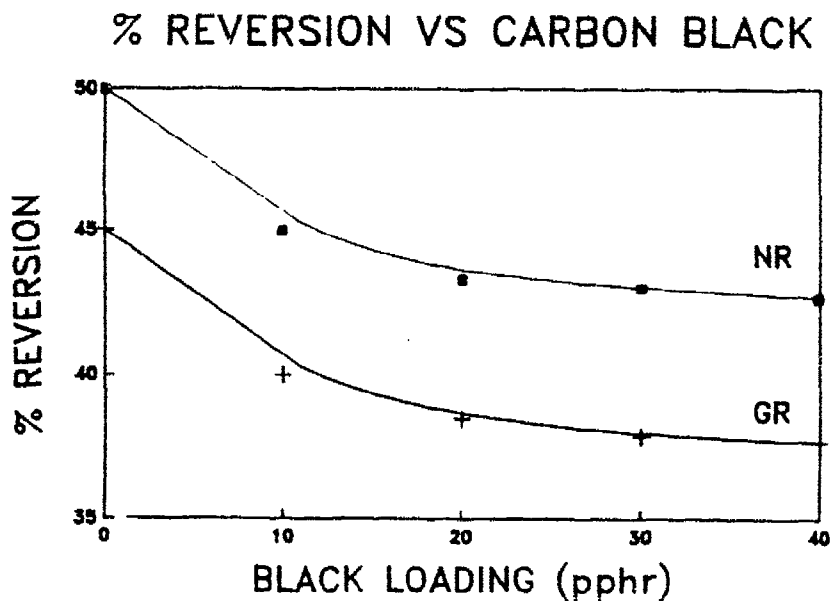
Figure 4. Plot showing the improvement in % Reversion versus carbon black
loading at 150°C. Reversion calculated 60 minutes after G'(max) is attained.

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The infrared spectra of carbon black filled natural rubber and guayule rubber as a function of curing time is shown in Figures 5 and 6, respectively. These samples contain 20 pphr carbon black and were cured at 150°C.
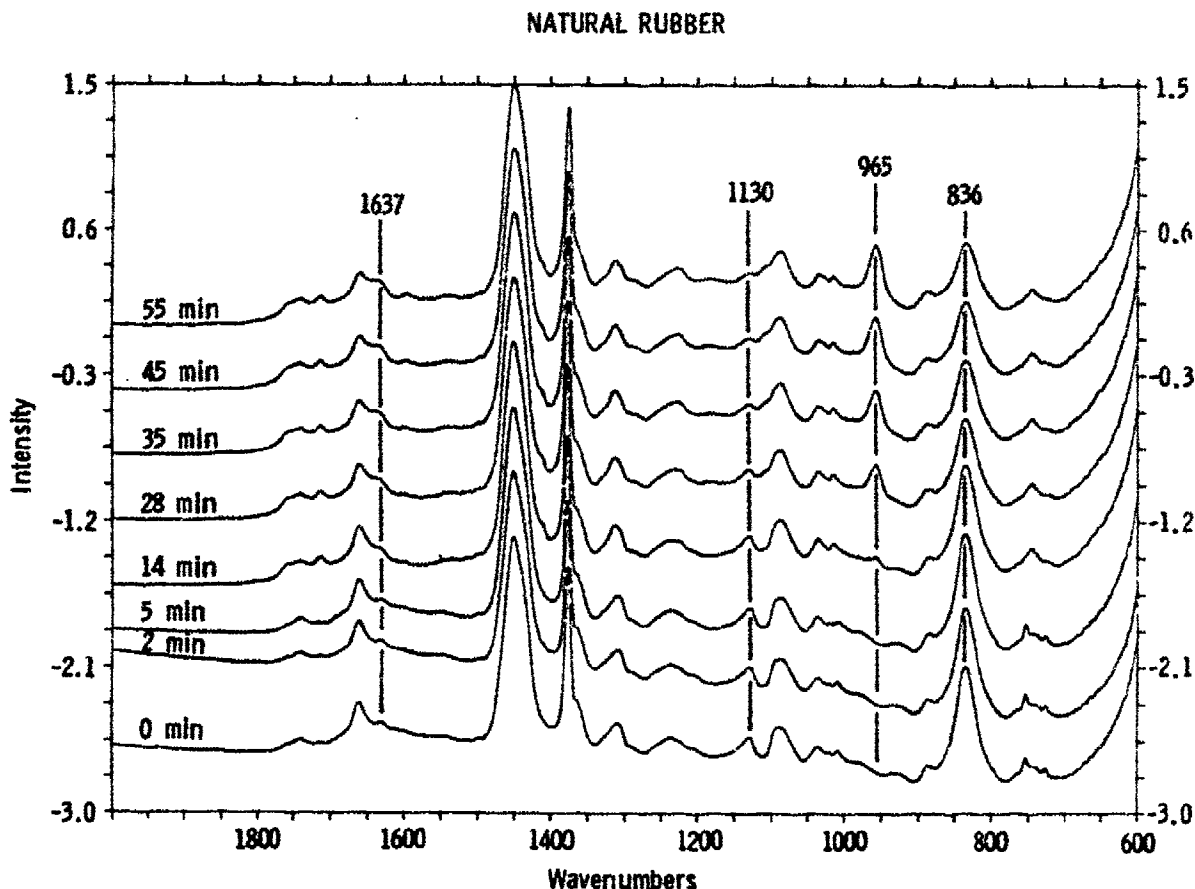
NATURAL RUBBER

Figure 5. FT-IR spectra obtained during the cure process for natural rubber at 150°C.

The initial spectra at time zero of the guayule rubber are identical to that of natural rubber with the exception of a larger 1720 cm^{-1} band in the guayule rubber sample. This is attributed to residual fatty acids that have not been completely extracted. As cure proceeds, both rubber systems show significant spectral changes. The intensity of the 965 cm^{-1} band increases as does the band at 1637 cm^{-1}. These bands have previously been assigned[7-9] to a trans-methine structure. The band at 836 cm^{-1} decreases with cure time. This is assigned to the C-H of the cis-methine. One can follow the change in intensity of these two bands as cure proceeds. Initially, no trans-methine is formed. This band is not detected until approximately seven minutes have passed.

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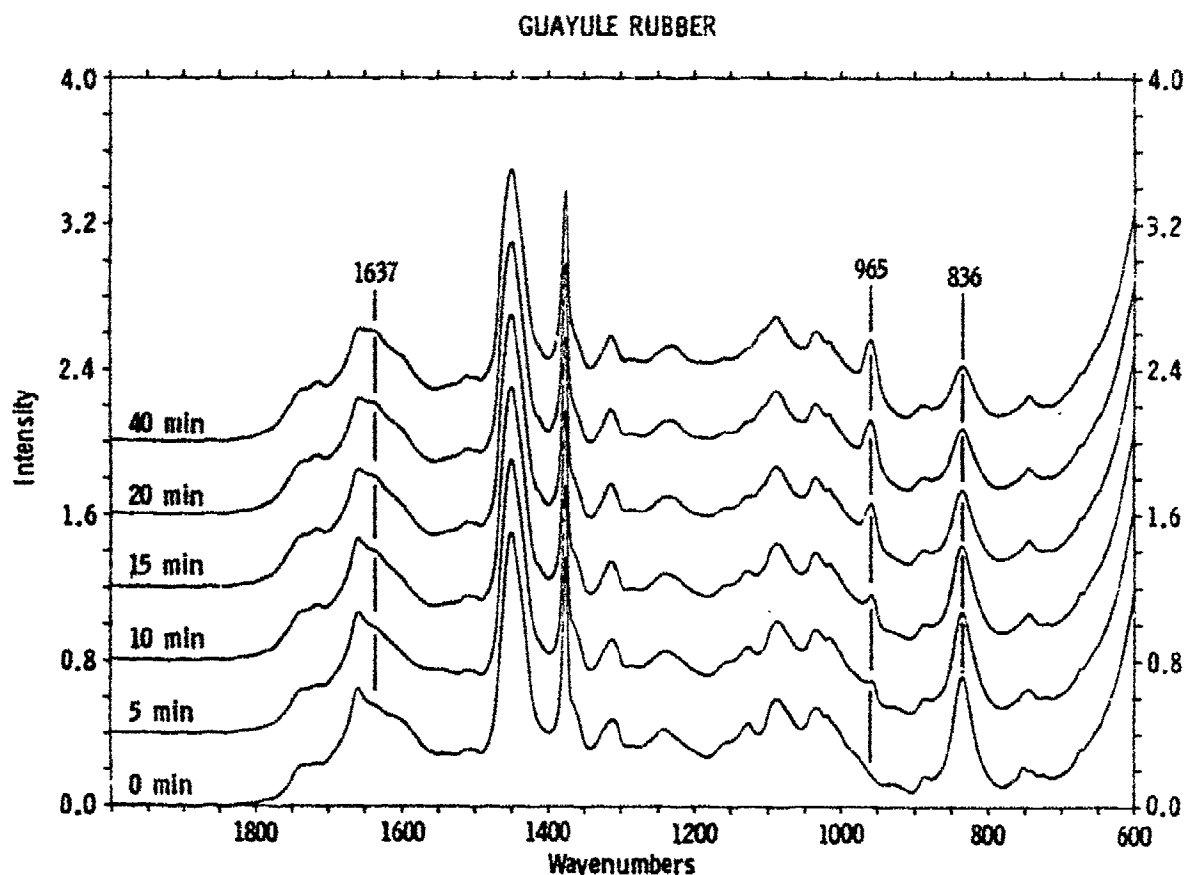
GUAYULE RUBBER

Figure 6. FT-IR spectra obtained during the cure process for guayule rubber at 150°C.

Figure 7 plots the appearance of the 965 cm^{-1} and the decrease of the 836 cm^{-1} bands. The curves appear to have similar shapes and exist as mirror images of one another. This effect is consistent with a concerted type reaction; i.e., when one structure leaves, the other appears.

The data from the mechanical spectrometer for the guayule sample are shown in Figure 8. The storage modulus G', a measure of rubber elasticity, shows a sharp increase as cure time proceeds. The G' value reaches a maximum and then slowly decreases. This portion of the curve with decreasing modulus is the effect of reversion. The appearance of the trans-methine structure at 965 cm^{-1} from the infrared spectra is shown on the same graph. From this plot it can be seen that the trans-methine content becomes detectable at approximately the same time as the mechanical reversion begins. This result clearly indicates that the changes occurring in the infrared spectra are due entirely to the reversion process and not to the vulcanization process. In fact, no changes are detected in the IR spectra during the vulcanization process. Both natural rubber and guayule rubber exhibit this effect.

7

IR KINETIC CHANGES FOR GUAYULE RUBBER
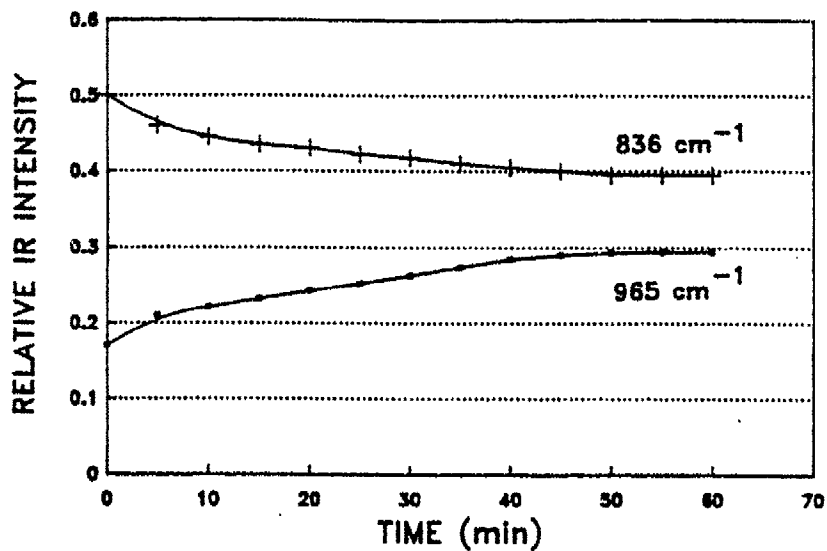
Figure 7. Plot of IR spectral changes during the mechanical
reversion process of guayule rubber at 150°C.
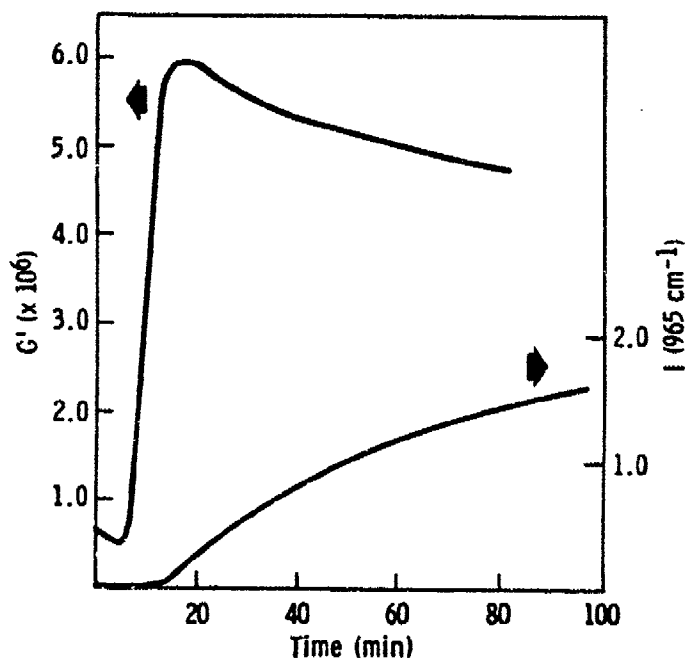
CURE AND REVERSION OF GUAYULE RUBBER

Figure 8. Graph showing the relationship between the mechanical and
IR spectra for 20 pphr carbon black filled guayule rubber at 150°C.
The intensity of the 965 cm^{-1} is a measure of the appearance of the
trans-methine structure.

8

CONCLUSION

Studies have been done on a series of natural rubber and guayule rubber compounds by employing Fourier transform infrared spectroscopy and dynamic mechanical analysis to characterize the cure and reversion behavior. The reversion process was found to be dependent on the amount of trans-methine structure formed during and after vulcanization. The appearance of these species coincided with the onset of mechanical reversion.

Two variables affecting cure and reversion have been studied: the amount of carbon black loading, and temperature of cure. It has been observed that reversion and $G'(max)$ were significantly affected by carbon black loading. An increase in loading showed a decrease in reversion and an increase in $G'(max)$. As the cure temperature was increased, an increase in the reversion process was also observed. For all samples studied, natural rubber exhibited more of a tendency to undergo reversion than identically formulated and cured guayule rubber samples.

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James M. Sloan

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Key Words

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Guayule rubber
Reversion

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